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DECARBONYLATION OF FURFURAL OVER OXIDE CATALYSTS

I. Investigation of Side Reaction Products

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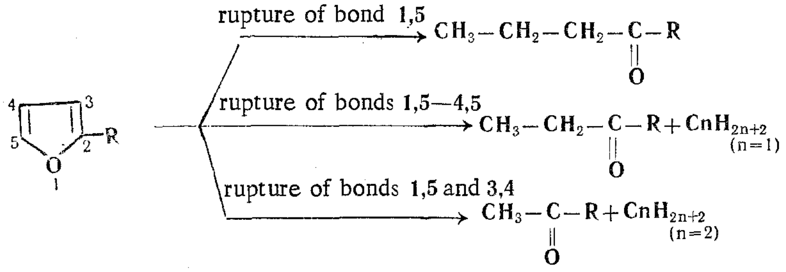
Gas chromatography has been used to investigate the products accompanying tetrahydrofuran prepared by hydrogenation of furan, without isolating the latter pure from the gas mixture obtained by decarbonylating furfural over oxide catalysts. A number of unknown impurities accompanying tetrahydrofuran and furan, are identified. It is found that tetrahydrofuran contains isopropanol, along with furan, α-methylfuran, and α-methyltetrahydrofuran. Furan itself contains α-methylfuran, and a number of unknown impurities, among them acetone. Ethane is found among the gaseous products of decarbonylation. Thus over Zn and Mn oxide catalysts there is joint hydrogenolysis of the furan ring, and ring opening at positions 1-5 and 3-4.

The tetrahydrofuran obtained by hydrogenating furan without separating it from the gaseous products of decarbonylation of furfural, contains various impurities, among them furan and butan-1-ol. These impurities are largely removed from tetrahydrofuran by fractional distillation. However, such purified tetrahydrofuran still contains impurities of hitherto undetermined nature, and the aim of the present work was to settle this problem.

In several papers [1-5] Shuikin and Bel'skii studied the hydrogenation of furan compounds over various catalysts. A nickel-alumina catalyst was studied in greatest detail, and at 140-150° it hydrogenated the furan ring, while at 200-275° the main reaction was joint hydrogenolysis of the latter. They showed that Raney Ni-alumina catalyst effects joint hydrogenolysis of the furan ring with formation of an aliphatic alcohol or ketone and an aliphatic hydrocarbon:



In the present paper gas chromatography has been used to investigate the products of decarbonylation of furfural over Zn and Mn oxide catalysts at 430°, and of hydrogenation of furan over Raney Ni at 120°.

A paper by Shuikin and Lebedev [6] describes the use of gas chromatography for analyzing mixtures of homologs of furan and tetrahydrofuran. Giller and coworkers [7] analyzed mixtures containing furan, alkylfurans, tetrahydrofuran, tetrahydropyran, dihydropyran, butan-1-ol, furfural, furfuryl alcohol, and tetrahydrofurfuryl alcohol. Polyakova, Sokolova, and Tsarfan [8] developed a chromatographic method for determining furan and butan-1-ol quantitatively when hydrogenating furan. However, α-methylfuran and α-methyltetrahydrofuran present could only be analyzed qualitatively. We have quantitatively analyzed mixtures of five known components (furan, α-methylfuran, tetrahydrofuran, α-methyltetrahydrofuran, and butan-1-ol). The study was made with different stationary liquid phases and with variation of the experimental parameters (column length, carrier gas flow rate, and column temperature were varied). A stationary phase of polypropyleneglycol-425 gave the best separation of the above components (Fig. 1). A LKhM-5 chromatograph made by the Special Construction Section, Chemical Divn. AS USSR, was used. The column measured 4 m × 3 mm, the packing was diatomaceous brick, grain size 0.25-0.5 mm, which was impregnated with 10% by weight of polypropyleneglycol-425, column temperature 65°, and the registering instrument had a response over the range 2-120 mV. The gas carrier (helium) flow was 3.5 l/hr. A butanol-free mixture took 25 min to analyze, one with butanol 2 hr, though 50 min at 90°. Internal standardization was used to determine the components quantitatively. Table 1 gives analytical results for artificial mixtures.

Internal standardization was used to check completeness of separation of the compounds. The standard compound chosen was toluene, which was added in various amounts to industrially prepared tetrahydrofuran. The data of Table 2 show that the amounts of toluene taken and found agree within the limits of practical error.

The method described was applied to an investigation of industrial grade tetrahydrofuran, and led to detection of

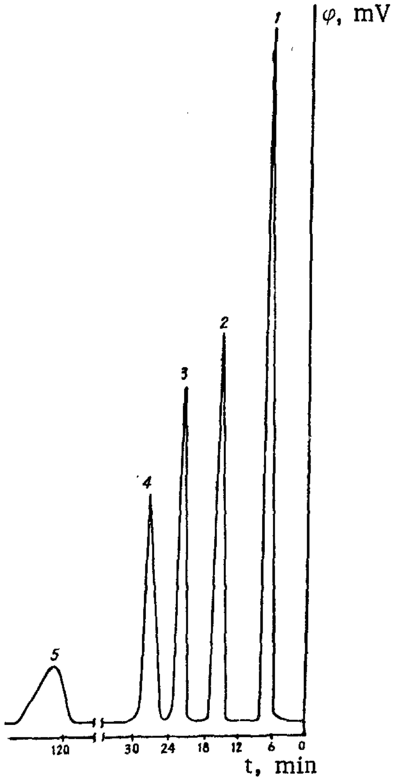


Fig. 1. Chromatogram of an artificial mixture: 1) furan; 2) ϑ-methylfuran; 3) tetrahydrofuran; 4) ϑ-methyltetrahydrofuran; 5) butan-1-ol.

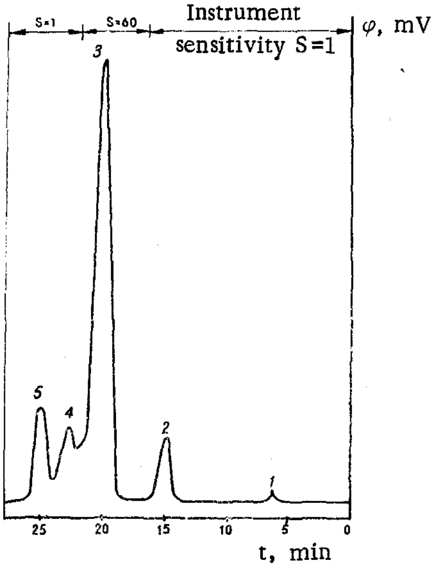


Fig. 2. Chromatogram of industrial tetrahydrofuran: 1) furan; 2) α-methylfuran; 3) tetrahydrofuran; 4) α-methyltetrahydrofuran; 5) isopropanol.

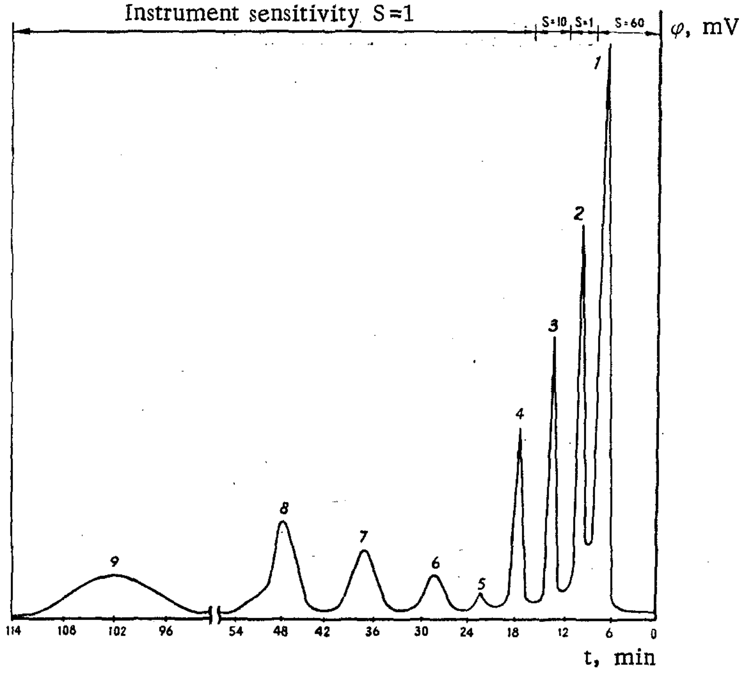


Fig. 3. Chromatogram of crude furan: 1) furan; 3) α-methylfuran; 2,4,5,6,7,8,9) unknown impurity.

an unknown impurity, with a retention time greater than that of α-methyltetrahydrofuran. The composition of the tetrahydrofuran was as follows: furan 0.01%, methylfuran 0.17%, tetrahydrofuran 99.05%, α-methyltetrahydrofuran 0.36%, unknown impurity 0.41% (Fig. 2). The retention time of the unknown impurity corresponded to isopropanol, and this identification was also supported by chemical evidence. Repeated distillation of the crude tetrahydrofuran through a 30-60 plate column gave a cut bp 77.3-77.4° (745 mm), having the composition α-methyltetrahydrofuran 71.25%, unknown impurity 28.75%. With phenyl isocyanate the fraction gave an urethane mp 86° (from petrol ether), mixed melting point with that derived from isopropanol undepressed. Further evidence for the presence of isopropanol in this fraction is the fact that the latter gives an IR absorption band at 3500 cm^{-1} corresponding to the valence vibrations of the hydroxyl group. So it can be considered as certain that the unknown impurity is isopropanol. Apparently it arises through joint hydrogenolysis of α-methylfuran and ring opening at position 1-5 and 3-4, followed by hydrogenation of the resultant acetone. To establish at which stage of the tetrahydrofuran preparation hydrogenolysis occurs, the impurity present in the furan was identified. The composition of the condensed crude furan was 88.43% furan, 7.21% α-methyl-

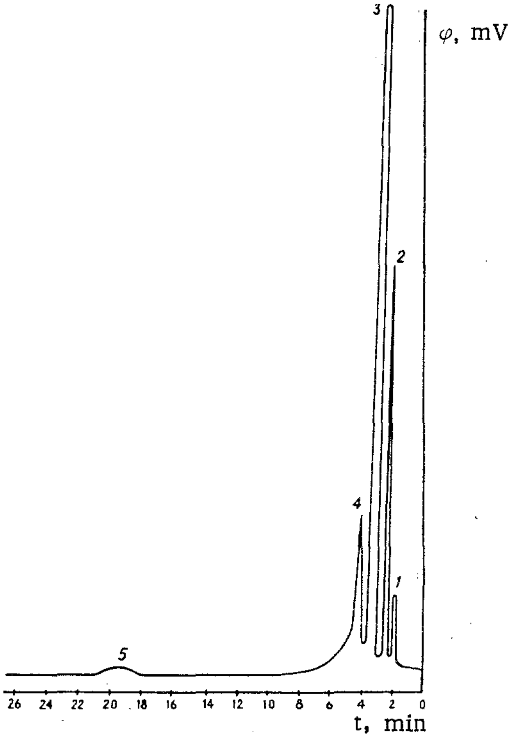


Fig. 4. Chromatogram of the gases from the decarbonylation of furan: 1) O_2; 2) N_2; 3) CH_4; 4) CO; 5) C_2H_6.

Table 1

Analyses of Artificial Mixtures

Mixture	Mixture components	Taken, %	Found, %	Absolute error %
I	Furan	0.44	0.40	−0.04
	α-Methylfuran	1.04	0.85	−0.19
	Tetrahydrofuran	93.29	93.54	+0.25
	α-Methyltetrahydrofuran	0.95	0.94	−0.01
	Butan-1-ol	4.28	4.27	−0.01
II	Furan	0.19	0.17	−0.02
	α-Methylfuran	0.44	0.37	−0.07
	Tetrahydrofuran	97.14	97.28	+0.14
	α-Methyltetrahydrofuran	0.40	0.42	+0.02
	Butan-1-ol	1.83	1.76	−0.07

furan, unknown impurity 4.36% (Fig. 3). The chromatogram shows that decarbonylation of furfural leads to formation of both furan and α-methylfuran. From the resultant crude furan there is obtained a cut boiling point 55° (750 mm), and a 2, 4-dinitrophenylhydrazone prepared from the fraction melted at 124° (ex ethanol), undepressed mixed melting point with authentic acetone 2, 4-dinitrophenylhydrazone. The retention time was the same as for acetone. Further, ethane was found in the decarbonylation gases (Fig. 4).

Table 2

Checking Completeness of Separation of Components by Internal Standardization

Run No.	Components	Taken, %	Found, %	Absolute error, %
1	Tetrahydrofuran*, Toluene	98.86 1.14	98.89 1.11	+0.03
2	Tetrahydrofuran*, Toluene	99.12 0.88	99.14 0.86	−0.02
3	Tetrahydrofuran*, Toluene	95.09 4.91	95.38 4.62	−0.29

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*The sample of tetrahydrofuran prepared industrially contained unknown amounts of the following impurities: furan, acetone, α-methylfuran, α-methyltetrahydrofuran, isopropanol.

The decarbonylation gases were analyzed by a method developed in NIIPM (The Scientific Research Institute for Plastics) [9] with a KhL-3 chromatograph using a column with CaX molecular sieves (column 1 m × 6 mm, column temperature 40°, carrier gas flow 2.5 l/hr, detector current 6 ma).

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